Introduction
to Ceramics
Second Edition

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the emulsion, the glass prevents loss of halogen from the silver halide particles).

8.3 Glass-Ceramic Materials

Glass-ceramic materials are produced by the controlled crystallization of appropriate glasses. They consist of a large proportion, typically 95 to 98 vol%, of very small crystals, generally smaller than 1 micron, with a small amount of residual glass phase making up a porefree composite.

When these materials are fabricated, bodies of desired shapes are formed with conventional glass-forming techniques. As discussed in Section 8.3, the conventional crystallization of glasses is almost invariably observed to initiate at the external surfaces, followed by the crystals growing into the amorphous phase and producing a nonuniform body of large grain size. For a variety of reasons, it is desirable that the crystals be small (less than 1 micron) and uniform in size. To obtain such small crystals occupying a large volume fraction of the material, a uniform density of nuclei of the order of 10^{12} to 10^{15} per cubic centimeter is required. Such copious nucleation is produced by adding selected nucleating agents to the batch during the melting operation and carrying out a controlled heat treatment.

The most commonly used nucleating agents are TiO_2 and ZrO_2, but P_2O_5, the Pt group and noble metals, and fluorides are also used. TiO_2 is often used in concentrations of 4 to 12 wt%; ZrO_2 is used in concentrations near its solubility limit (4 to 5 wt% in most silicate melts). In some cases, ZrO_2 and TiO_2 are used in combination to obtain desired properties in the final crystallized bodies.

The Pt group and noble metal nucleating agents seem to function by directly forming a crystalline nucleating phase in a precipitation process. The major crystalline phase or phases subsequently grow on particles of the nucleating phase. Such a process could also be operative in the case of oxide nucleating agents, but in many cases these melt additions seem to be effective in promoting a phase-separation process. The separation can provide a fine dispersion of second-phase material, which can then form a crystalline nucleant phase.

The role of phase separation in the nucleation process has been associated with a number of factors, including (1) the formation of an amorphous phase of relatively high mobility in a temperature range in which the driving force for crystallization is large. From such a phase, crystal nucleation can occur rapidly. (2) The introduction of second-phase boundaries between the phase-separated regions on which the nucleation of the first crystalline phase may take place. (3) The provision of a driving

force for crystallization in cases in which no such driving force exists for the homogeneous solution. Of these possibilities, the first seems to be the most important and the most generally applicable.

Direct experimental evidence on the precise role of oxide nucleating agents is rather meager. In one study of a TiO_2-nucleated $Li_2O–Al_2O_3–SiO_2$ glass-ceramic, the nucleation stage consisted of phase separation on a scale of about 50 Å followed by the formation of a crystalline TiO_2-rich nucleating phase. This phase was estimated to contain about 35 wt% Ti and about 20 wt% Al; the starting material contained less than 5 wt% TiO_2. In other similar systems, however, there is no evidence of structural heterogeneities, detectable by either electron-microscope or light-scattering observations, prior to the appearance of the crystals of the major phases. This could reflect different modes of nucleation being effective in different systems or merely indicate the difficulties of detecting small-scale heterogeneities. More generally, it should be noted that the important oxide nucleating agents are of great use in a number of systems containing sizable concentrations of SiO_2 and often significant amounts of Al_2O_3 as well. In contrast, for many other systems—for example, many phosphate-based systems—they are not at all effective. The differences seem most likely associated with differences in immiscibility behavior but might also reflect differences in lattice match of possible crystalline phases as well.

The steps used in processing a glass-ceramic body are illustrated schematically by the temperature-time cycle shown in Fig. 8.27. The material is melted and formed at elevated temperatures and then often
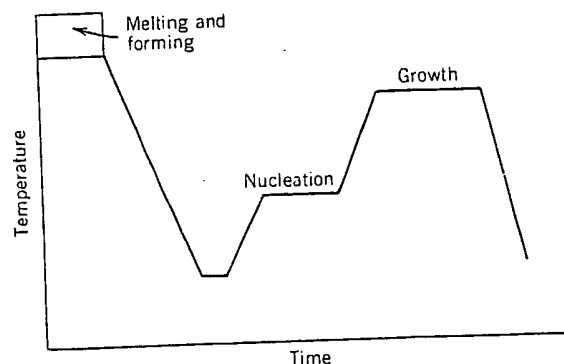

Fig. 8.27. Schematic temperature-time cycle for the controlled crystallization of a glass-ceramic body.

cooled to ambient, at which additional processing steps may be carried out. The material at this stage may be largely homogeneous, or it may contain some phase-separated domains or some very small crystals of the nucleant phase.

The sample is then heated at a rate limited by the avoidance of thermal shock to a holding temperature at which nucleation of the major phases is effected. The sample is typically held at this nucleation temperature, at which the melt viscosity is often in the range of 10^{11} to 10^{12} P, for 1 to 2 hr. The scale of formation of the initial nuclei is often in the range of 30 to 70 Å (see Fig. 8.28 as an example).

After nucleation is completed, the material is heated further to effect the growth of the major crystalline phases. The maximum temperature for growth is generally chosen to maximize the kinetics of crystal growth, subject to the constraints of obtaining the desired combination of phases and avoiding deformation of the sample or unwanted transformations within the crystalline phases or redissolution of some of the phases. This temperature and the time for which the material is held at the temperature, which can be very brief, depend on the system and composition as well as on the phases and properties desired in the final body.

In most cases the crystallization is carried out to a fraction crystallized exceeding 90% and often exceeding 98%. The final grain size is typically in the range of 0.1 to 1 micron. This is considerably smaller than the grain size of conventional ceramic bodies, illustrated by the micrographs in Chapter 11.

The volume fractions of the various phases, both crystalline and glassy, in a glass-ceramic body are determined by the composition of the initial

0.1 μ

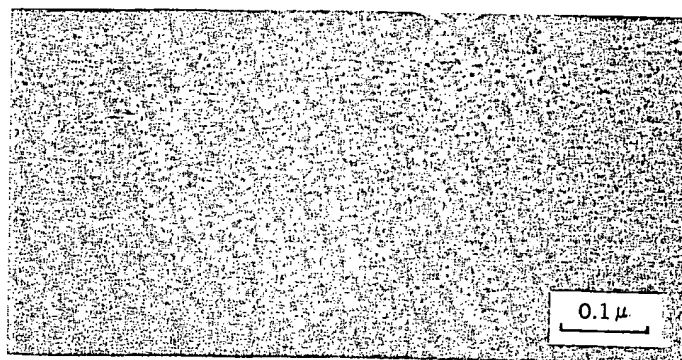Fig. 8.28.   Crystalline nuclei in $Li_2O–Al_2O_3–SiO_2$ composition with 4% TiO_2 addition. From G. H. Beall in L. L. Hench and S. W. Freiman, Eds., *Advances in Nucleation and Crystallization in Glasses*, American Ceramic Society, 1972, pp. 251–261.

glass, the stoichiometry of the crystalline phases, and the temperatures and times of the crystallization treatment. Metastable phases are often encountered, however, and both the final assemblage of phases and the sequence of microstructural development depend in general on details of the crystallization heat treatment and its relation to the kinetics of the nucleation and crystal growth processes.

As examples of the variation in crystal size which can be achieved by variations in the heat-treatment cycle, consider the composition studied by Doherty and his associates:* SiO_2, 70 wt%; Al_2O_3, 18%; MgO, 3%; Li_2O, 3%; and TiO_2, 5%. The TiO_2-rich nuclei, estimated to contain about 35 wt% Ti, begin to form at temperatures about 725°C; their rate of formation reaches a maximum between 800 and 825°C and becomes quite small again at temperatures in the range of 850°C. The major crystalline phase, *β-eucryptite*, forms on the TiO_2-rich nuclei and subsequently transforms to *β-spodumene* at temperatures above 1000°C. The growth rate of the eucryptite crystals becomes significant at temperatures about 825°C and increases with increasing temperature over a range above this. This knowledge of the kinetics of nucleation and growth can be used to control the microstructure by controlling the heat treatment. Examples of such control are given in Figs. 8.29 and 8.30. Figure 8.29 shows a sample which was heated rapidly to 875°C and held for 25 min. Because it was heated rapidly through the region of rapid nucleation, relatively few nuclei formed, and large eucryptite crystals, in the range of several microns, result. The same composition held at 775°C for 2 hr and then heated to 975°C for 2 min is characterized by an appreciably smaller crystal size, in the range of 0.1 micron (Fig. 8.30).

Important Glass-Ceramic Systems. Among the systems in which technologically important glass-ceramic materials have been produced, the following seem most noteworthy:

(1) $Li_2O-Al_2O_3-SiO_2$. This system is by far the most important commercial system. It is used for glass-ceramic materials having very low thermal expansion coefficients and hence very high resistance to thermal shock. Among the trade names for materials in this system and Corning's Corning Ware, Owens-Illinois' Cer-Vit, and PPG's Hercuvit. The very low expansion coefficients in this system, which in some cases are appreciably lower than that of fused silica, are associated with the presence in the crystallized materials of crystalline β-spodumene ($Li_2O·Al_2O_3·4SiO$), which has a low expansion coefficient, or β-eucryptite ($Li_2O·Al_2O·2SiO_2$), which has an expansion coefficient that is larger in

*P. E. Doherty in R. M. Fulrath and J. A. Pask, Eds., *Ceramic Microstructures*, John Wiley & Sons, Inc., New York, 1968.
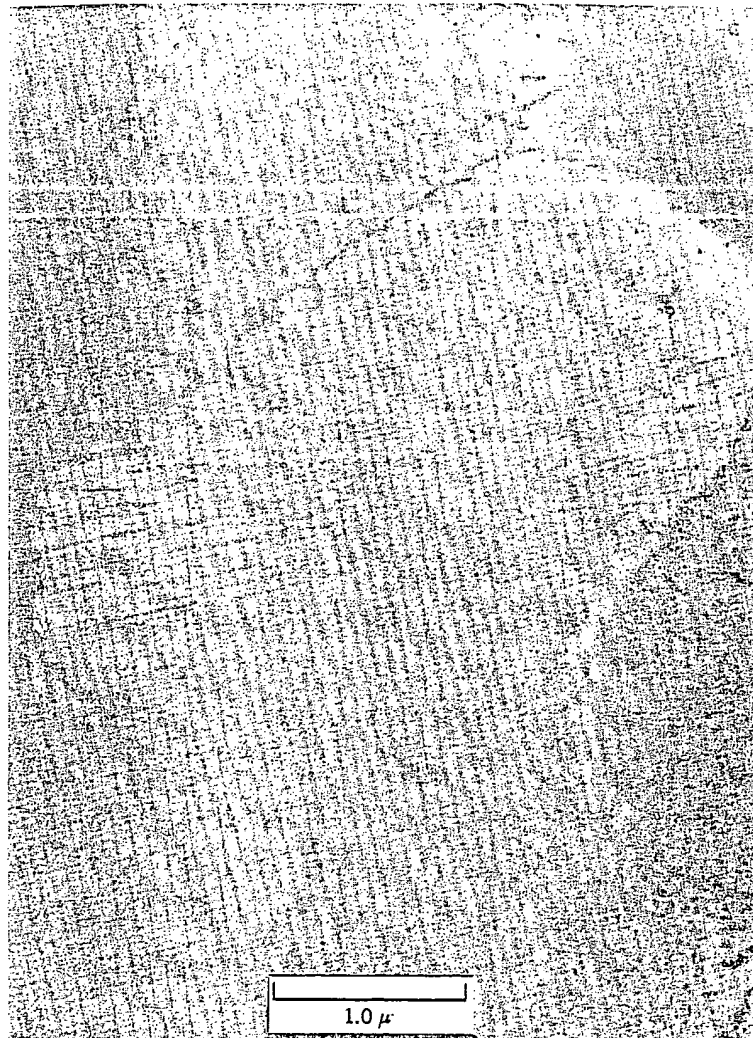
Fig. 8.29.   Submicrostructure in Li_2O–Al_2O_3–SiO_2 glass-ceramic heated rapidly to 875°C and held for 25 min. From P. E. Doherty in R. M. Fulrath and J. A. Pask, Eds., *Ceramic Microstructures*, John Wiley & Sons, Inc., New York, 1968, pp. 161–185.

magnitude and negative. Commercial compositions are found in several ranges in this system. Among them are the following (in weight percent): Li_2O (2.6), Al_2O_3 (18), SiO_2 (70), and TiO_2 (4.5). Different phase assemblages, characterized by different sets of properties, can result from using TiO_2 and ZrO_2 in varying proportions as the nucleating agent.
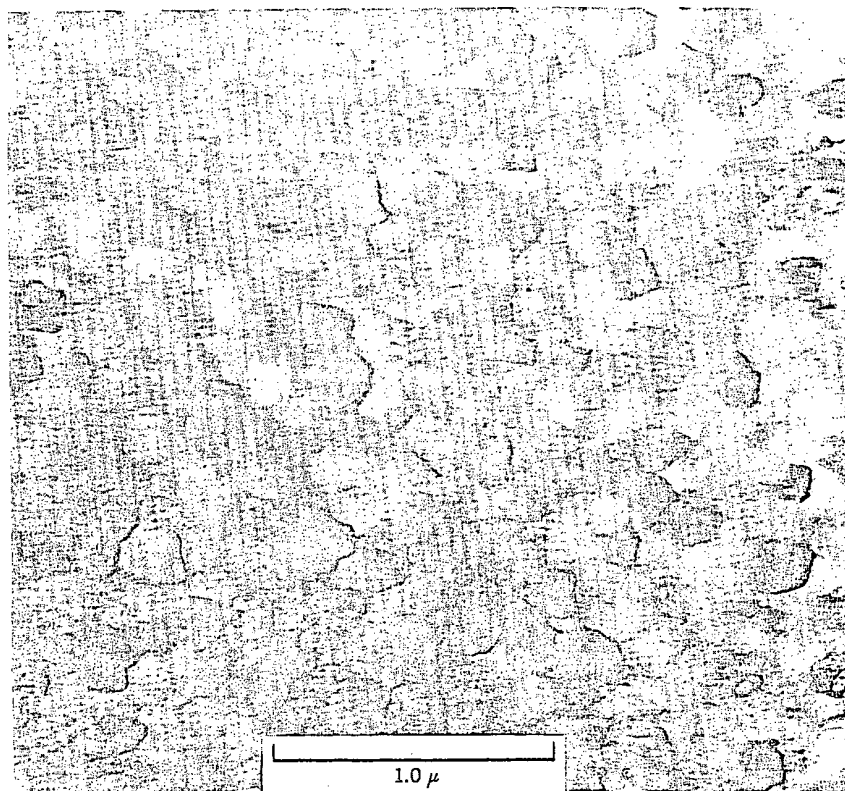
Fig. 8.30. Submicrostructure in $Li_2O-Al_2O_3-SiO_2$ glass-ceramic, having identical composition with that shown in Fig. 8.29, held at 775°C for 2 hr before heating to 975°C for 2 min. From P. E. Doherty in R. M. Fulrath and J. A. Pask, Eds., *Ceramic Microstructures*, John Wiley & Sons, Inc., New York, 1968, pp. 161–185.

(2) $MgO-Al_2O_3-SiO_2$. This system forms glass-ceramic materials having high electrical resistivity and high mechanical strength. The high strength has been associated with the presence in the crystallized materials of crystalline β-cordierite ($2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$). The compositions of some useful glass-ceramic materials in this system cover a range about MgO (13), Al_2O_3 (30), SiO_2 (47), and TiO_2 (10).

(3) $Na_2O-BaO-Al_2O_3-SiO_2$. Commercial glass-ceramic materials in this system have thermal expansion coefficients in the range of 80×10^{-7} per degree centigrade and cover a range of composition about Na_2O (13), BaO (9), Al_2O_3 (29), SiO_2 (41), and TiO_2 (7). The important crystalline phases are nepheline ($Na_2O \cdot Al_2O_3 \cdot 2SiO_2$) and celsian ($BaO \cdot Al_2O_3 \cdot 2SiO_2$). In practice, the commercial products based on this system, most notably

Corning's Centura Ware, use a compressive glaze to achieve desired mechanical strengths. The use of such glazes is discussed in Chapter 16.

(4) $Li_2O-MgO-Al_2O_3-SiO_2$. Glass-ceramic materials in this system are noted for their variable, in some cases low or negative, thermal expansion coefficients, transparency (in some cases), and the ease with which they can be chemically strengthened. The important crystalline phase is a stuffed β-quartz solid solution.

(5) $K_2O-MgO-Al_2O_3-SiO_2$. Glass-ceramic materials in this system are melted with small concentrations of fluoride and are noted for the quality of machinability. This characteristic is associated with the presence of mica phases having large aspect ratios in the crystallized bodies.

Properties of Glass-Ceramic Materials. The principal advantages of glass-ceramic materials over conventional ceramics are associated with the economy and precision of the forming operations, with the absence of porosity in the materials, and with the occurrence of well-dispersed, very small crystals having desirable properties in the crystallized bodies. The absence of porosity is related to the relatively small volume changes involved in crystallizing these systems and to the fact that changes in volume can be accommodated by flow. The small crystal size is a result of copious nucleation achieved by adding the nucleant to the melt. The particular material properties can to a significant extent be programmed by the selection of a suitable composition and crystallization treatment. This last factor constitutes perhaps the essential feature of the glass-ceramic concept, namely, the achievement of desired properties or combinations of properties by a systematic variation of the chemistry and microstructure of materials containing both glassy and crystalline phases. This variation in turn is effected by means of a controlled crystallization treatment; its systematic feature is made possible by the continuous and wide-ranging variation of phase assemblages which can be achieved in glass-and-ceramic bodies (in contrast to the more restricted range possible with crystalline ceramics).

In some cases, a glass-ceramic material is not designed for its properties in the as-crystallized state but rather for the ease with which postcrystallization treatments can be effected. An example is the development of glass-ceramic materials whose surfaces can easily be strengthened by cladding or by an ion-exchange process. The latter development can be particularly complex, since the ion-exchange treatment of a glass-ceramic body includes not only the direct strengthening of the glass phase or phases by a stuffing process, as discussed in Chapter 16, but also more important effects which involve the crystalline phases as well: phase transformations to phases of different volumes and expansion coefficients, and solid solution in the already existing crystalline phases, changing their volumes and expansion coefficients.

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